

TITLE OF THE INVENTION  
CHEMICAL TREATMENT METHOD AND CHEMICAL TREATMENT  
APPARATUS

CROSS-REFERENCE TO RELATED APPLICATION

5           This application is based upon and claims the  
benefit of priority from the prior Japanese Patent  
Application No. 2002-240452, filed August 21, 2002, the  
entire contents of which are incorporated herein by  
reference.

10                           BACKGROUND OF THE INVENTION

1.   Field of the Invention

          The present invention relates to a chemical  
treatment method and chemical treatment apparatus by  
which a metal film formed on a material to be subjected  
15   to film formation is etched into a predetermined  
pattern.

2.   Description of the Related Art

          A TAB (Tape Automated Bonding) technique has  
attracted attention for a long time as a assembling  
20   technique for assembling semiconductor chips on a long  
and flexible carrier tape. This TAB technique is very  
useful since three-dimensional assembling can be  
performed by using the flexibility of the carrier tape  
and a plurality of semiconductor chips can be assembled  
25   on the same carrier tape.

          On a carrier tape to be applied to the TAB  
technique, various wiring patterns made of metals such

as gold and copper are formed to allow electrical connection to semiconductor chips. Carrier tapes of this type are classified into "two-layered carrier tape" on which a metal film is directly formed by sputtering or the like without any adhesive, and "three-layered carrier tape" on which a metal foil is adhered by means of an adhesive. Compared to the three-layered carrier tape, the two-layered carrier tape has excellent electrical characteristics and can increase the processing speed of a semiconductor chip because no adhesive is used. Therefore, the two-layered carrier tape is the most popular carrier tape recently.

In this two-layered carrier tape, a metal undercoating is formed between the tape and the metal film to increase the adhesion between them. FIG. 1 shows metals often used as metal undercoatings and the principal characteristics of these metal undercoatings.

As shown in FIG. 1, any of copper, a nickel-chromium-based metal, a nickel-vanadium-based metal, and a chromium-based metal as metal undercoatings has a sufficient initial strength when judged from viewpoints of, e.g., mechanical characteristics, chemical stability, and electrical conductivity. Of these metal undercoatings, copper, nickel-chromium-based metal, and nickel-vanadium-based

metal are unstable and easily deteriorate in  
a high-temperature environment and high-humidity  
environment, and are also unsuited to gold plating  
using a cyanide gold plating solution. However, these  
5 three metal undercoatings can be readily etched into  
a predetermined pattern.

Compared to the above three metal undercoatings,  
a chromium-based metal has resistance to  
a high-temperature environment and high-humidity  
10 environment. In addition, a chromium-based metal can  
be well subjected to gold plating using a cyanide gold  
plating solution.

Unfortunately, this chromium-based metal must  
be etched by a special etching method in  
15 a high-temperature, and the metal must be treated by  
harmful treatment solutions such as potassium  
permanganate. This places a load on the environment  
when waste solution disposal is performed, and produces  
hexavalent chromium whose disposal is more and more  
20 strictly regulated in recent years. That is, a number  
of various unfavorable conditions occur. Accordingly,  
a chromium-based metal is unsuited to etching.  
Therefore, a chemical treatment method and chemical  
treatment apparatus capable of easily etching these  
25 metals are demanded.

#### BRIEF SUMMARY OF THE INVENTION

It is an object of the present invention to

provide a chemical treatment method capable of easily etching metals, particularly chromium, unsuited to etching, and a chemical treatment apparatus using this chemical treatment method.

5           The present invention is a chemical treatment method and chemical treatment apparatus by which a metal film formed on a material to be subjected to film formation is etched into a predetermined pattern. According to a first aspect of the present invention,  
10           an electrolysis reduction treatment is performed for a metal film as a cathode by using one of an acidic treatment solution containing acid radicals and an alkaline treatment solution containing halogen ions. The metal film is then dipped in another acidic  
15           treatment solution. Preferred examples of the acidic treatment solution containing acid radicals are hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), carboxylic acid (RCOOH), hydrogen fluoride (HF), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). Preferred examples of the  
20           halogen ions are sodium chloride (NaCl), potassium chloride (KCl), and potassium iodide (KI). Preferably, another acidic treatment solution contains halogen ions.

          According to a second aspect of the present  
25           invention, an electrolysis reduction treatment is performed for a metal film as a cathode in a treatment solution containing chloride ions. The metal film is

then dipped in an acidic treatment solution. This acidic treatment solution preferably contains halogen ions.

5 In the present invention as described above, a metal film formed on a material to be subjected to film formation can be etched into a predetermined pattern by simple processes, i.e., by reducing an oxide formed on the surface of the metal film by an electrolysis reduction treatment, and performing  
10 an acid dip process after that.

As a metal forming the metal film, one of chromium, titanium, tungsten, palladium, and molybdenum is used. Also an alloy containing at least one of chromium, titanium, tungsten, palladium, and molybdenum  
15 is used. As the alloy, nickel chrome alloy is preferably used. Especially when the metal film contains chromium, the production of hexavalent chromium can be prevented.

In the electrolysis reduction treatment, the metal  
20 film may also be partially dipped in a treatment solution containing chloride ions. In this case, the metal film need not be entirely dipped in the treatment solution, e.g., it is only necessary to partially dip the metal film into the treatment solution. Since this  
25 reduces the amount of treatment solution used, the treatment solution used can be saved.

In the electrolysis reduction treatment, it is

also possible to dip a metal film in an acidic treatment solution containing halogen ions, preferably, an acidic treatment solution containing chloride ions, and perform electrolysis reduction for the metal film as a cathode. Since electrolysis reduction is performed for the metal film as a cathode while the metal film is dipped in an acidic treatment solution containing halogen ions, preferably, an acidic treatment solution containing chloride ions, the metal film can be easily etched into a predetermined pattern while an oxide formed on the surface of the metal film is reduced.

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention and, together with the production description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a table showing metals often used as metal undercoatings and the principal characteristics of these metal undercoatings;

5       FIG. 2A is a sectional view showing an example of a material to be subjected to film formation by a chemical treatment method according to an embodiment of the present invention;

10       FIG. 2B is a sectional view showing an example of the material shown in FIG. 2A which is coated with a photoresist;

FIG. 2C is a sectional view showing an example of the state in which the material shown in FIG. 2B is exposed via a photomask;

15       FIG. 2D is a sectional view showing an example of the material on which a resist pattern is formed;

FIG. 2E is a sectional view showing an example of the material on which a copper film is etched in accordance with the resist pattern;

20       FIG. 2F is a sectional view showing an example of the material on which a chromium film is etched from the state shown in FIG. 2E;

FIG. 2G is a sectional view showing an example of the material from which the photoresist is removed from the state shown in FIG. 2F;

25       FIG. 3A is a schematic view showing the principle of a cathode electrolysis reduction treatment;

FIG. 3B is a schematic view showing the principle

of the cathode electrolysis reduction treatment;

FIG. 3C is a schematic view showing the principle of an acid dip treatment;

FIG. 4 is a schematic view showing the principle  
5 of an acid electrolysis treatment;

FIG. 5 is a schematic side sectional view showing an example of a vertical feed type chemical treatment apparatus;

FIG. 6 is a schematic front sectional view showing  
10 a cathode electrolysis reduction device forming the chemical treatment apparatus shown in FIG. 5;

FIG. 7 is a schematic side sectional view showing an example of the chemical treatment apparatus;

FIG. 8 is a schematic side sectional view showing  
15 an example of a horizontal feed type chemical treatment apparatus;

FIG. 9 is a schematic side sectional view showing an example of a chemical treatment apparatus;

FIG. 10 is a longitudinal side sectional view  
20 showing an example of a cathode electrolysis reduction device;

FIG. 11 is a longitudinal side sectional view showing an example of an acid dip device;

FIG. 12 is a longitudinal side sectional view  
25 showing an example of an electrolysis device of the chemical treatment apparatus;

FIG. 13 is a table showing the test results of the



etching states of a copper film and chromium film when treatment conditions are changed in each treatment according to the chemical treatment method;

FIG. 14 is a table showing the test results of the etching states of a chromium film when various conditions of Experiment No. 7 shown in FIG. 13 are changed;

FIG. 15 is a table showing the results of a test conducted to check whether chromium reduction occurs on the surface of a chromium film under the influence of an acidic treatment solution containing chloride ions during a cathode electrolysis reduction process;

FIG. 16 is a table showing the results of a pH dependence test conducted to check whether a chromium film is etched by a treatment solution during the cathode electrolysis reduction process; and

FIG. 17 is a table showing the results of a test conducted to check whether hexavalent chromium exists in treatment solutions in an acid dip process when hydrochloric acid, sulfuric acid, and an NaCl solution are used as the treatment solutions.

#### DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the present invention will be described below with reference to the accompanying drawing. However, the scope of the invention is not limited to these embodiments shown in the drawing.

First and second chemical treatment methods of the

present invention will be separately explained below.  
FIGS. 2A to 2G are sectional views each showing  
an example of the state of a metal film on a material  
to be subjected to film formation, in each process of  
5 a chemical treatment method according to an embodiment  
of the present invention.

[First Chemical Treatment Method]

First, as shown in FIG. 2A, a chromium film 120  
having a predetermined film thickness is formed by  
10 sputtering or the like on one surface of a material 110  
to be subjected to film formation. On the chromium  
film 120, a copper film 130 having a predetermined film  
thickness is formed by sputtering or the like. In this  
manner, a material 100 to be treated is obtained.  
15 As the material 110, it is possible to use a sheet-like  
or carrier-tape-like flexible substrate made of, e.g.,  
polyimide, glass epoxy, BT (Bismaleimide Triazine)  
resin, or polyester, or a semiconductor wafer made of,  
e.g., silicon.

20 After that, as shown in FIG. 2B, the copper film  
130 is coated with a photoresist 140. In addition, as  
shown in FIG. 2C, the photoresist 140 is exposed  
through a photomask 150 and developed with a  
predetermined developer. By this treatment, as shown  
25 in FIG. 2D, a predetermined resist pattern is formed on  
the copper film 130.

The material 100 shown in FIG. 2D is dipped in

a predetermined treatment solution to wet-etch the copper film 130, and the material 100 is washed.

This treatment will be referred to as "a copper wet etching treatment" hereinafter, and a process of

5 performing this treatment will be referred to as

"a copper wet etching process" hereinafter.

Consequently, as shown in FIG. 2E, the material 100

on which the copper film 130 is etched into

a predetermined pattern in accordance with the resist

10 pattern is obtained.

After that, the material 100 shown in FIG. 2E is used as a cathode to perform electrolysis reduction by nascent hydrogen for the chromium film 120 by using

a predetermined treatment solution. This electrolysis

15 reduction treatment will be referred to as "a cathode

electrolysis reduction treatment" hereinafter, and

a process of performing this treatment will be

referred to as "a cathode electrolysis reduction

process" hereinafter. A treatment solution of this

20 cathode electrolysis reduction treatment is one of

an acidic treatment solution containing an acid

radical and an alkaline treatment solution containing

halogen ion. A treatment solution is preferably

an acid-radical-containing acidic treatment solution,

25 e.g., hydrochloric acid, sulfuric acid, carboxylic

acid, or hydrogen fluoride. For example,

a chloride-ion-containing treatment solution such as

SAS manufactured by K.K. MURATA is used.

FIGS. 3A and 3B are schematic views showing the principle of the cathode electrolysis reduction treatment. In this cathode electrolysis reduction treatment, as shown in FIG. 3A, the material 100 used as a cathode can be entirely dipped in a treatment solution 24 contained in a vessel 20, together with an electrode plate 22 used as a positive electrode. As shown in FIG. 3B, the electrode plate 22 and material 100 may also be partially dipped in the treatment solution 24. For example, by wet etching process, the chromium film 120 has passivated itself by forming a chromium oxide film on its surface. Therefore, In the cathode electrolysis reduction process, this oxide film is reduced to metal chromium. The material 100 subjected to this cathode electrolysis reduction treatment is washed with deionized water.

After that, a dip treatment of the chromium film 120 is performed by dipping the material 100 in a predetermined treatment solution 24 for a predetermined time. This dip treatment will be referred to as "an acid dip treatment" hereinafter, and a process of performing this treatment will be referred to as "an acid dip process" hereinafter.

A treatment solution used in this acid dip treatment is an acidic treatment solution containing halogen ion, preferably, an acidic treatment solution

containing chloride ion. An example of this acidic treatment solution is SAS manufactured by K.K. MURATA.

Concentration of the treatment solution 26 of the acid dip treatment is denser than that of the treatment solution used in the cathode electrolysis reduction treatment described above. FIG. 3C is a schematic view showing the principle of the acid dip treatment. As shown in FIG. 2F, by performing this acid dip treatment having the principle as shown in FIG. 3C, the chromium film 120 of the material 100 can be etched into a predetermined pattern without giving any damage to the surface of the material 110.

The material 100 shown in FIG. 2F is then washed with deionized water, and the photoresist 140 remaining on the material 100 is removed by using a predetermined treatment solution. The material 100 from which the photoresist 140 is thus removed is washed and dried.

Through the individual processes described above, as shown in FIG. 2G, the chromium film 120 and copper film 130 formed on the material 110 can be etched into a predetermined pattern in accordance with the resist pattern.

In the first chemical treatment method as described above, the chromium film 120 formed on the material 110 can be etched into a predetermined pattern by performing the cathode electrolysis reduction process and acid dip process in this order, i.e.,

by combining simple processes. Also, the production of hexavalent chromium can be prevented. This results in the advantage that waste solution disposal of each treatment solution can be easily performed.

5           In addition to the prevention of the production of hexavalent chromium, the chromium film 120 can be etched without using any cyanide compound as a treatment solution in each of the cathode electrolysis reduction process and acid dip process.  
10       This greatly reduces the labor of waste solution disposal compared to the conventional method. Also, relatively inexpensive chloride-based chemicals such as hydrochloric acid, a NaCl solution, and SAS manufactured by K.K. MURATA can be used as treatment  
15       solutions in the cathode electrolysis reduction treatment and acid dip treatment. Since the chromium film 120 can be etched by using these treatment solutions, the cost of chromium etching can be greatly reduced.

20       [Second Chemical Treatment Method]

          A material 100 to be treated shown in FIG. 2E is obtained by performing the same treatments as in the first chemical treatment method described above. After that, as shown in FIG. 4, the material 100 and  
25       an electrode plate 22 as a positive electrode are dipped in a predetermined treatment solution 28 contained in a vessel 20. In this state, the material

100 is used as a cathode to perform electrolysis reduction for a chromium film 120 in the treatment solution 28. This electrolysis reduction treatment will be referred to as "an acid electrolysis treatment" hereinafter, and a process of performing this treatment will be referred to as "an acid electrolysis process" hereinafter. The treatment solution 28 of this acid electrolysis treatment is an acidic treatment solution containing halogen ion, preferably, a chloride-ion-containing acidic treatment solution such as SAS manufactured by K.K. MURATA.

By this acid electrolysis treatment, the chromium film 120 can be etched into a predetermined pattern as shown in FIG. 2F, while a chromium oxide film formed on the surface of the chromium film 120 is reduced. After that, the same treatments as in the first chemical treatment method are performed to obtain a material 100 shown in FIG. 2G.

In the second chemical treatment method as described above, the chromium film 120 formed on the material 110 to be subjected to film formation can be etched into a predetermined pattern through a simple process, i.e., the acid electrolysis treatment, and the production of hexavalent chromium can also be prevented. Additionally, in the second chemical treatment method, two processes of the cathode electrolysis reduction treatment and acid dip treatment

in the first chemical treatment method can be performed  
by one process of the acid electrolysis treatment.  
The two processes of the cathode electrolysis reduction  
treatment and acid dip treatment include a washing  
5 treatment between these processes. Therefore, the  
labor of this washing treatment can be saved by  
performing only the process of the acid electrolysis  
treatment.

In the first and second chemical treatment  
10 methods, the chromium film 120 is etched. However,  
the present invention is not limited to chromium.  
For example, even when titanium, tungsten, palladium,  
and molybdenum are used, the chemical treatment methods  
of the present invention can etch these metals into  
15 a predetermined pattern. Also even when an alloy  
containing at least one of chromium, titanium,  
tungsten, palladium, and molybdenum is used, the  
chemical treatment methods of the present invention can  
etch the alloy into a predetermined pattern. As the  
20 alloy, nickel chrome alloy is preferably used.

Next, [Application Example 1] to [Application  
Example 6] will be separately described below as  
application examples of various chemical treatment  
apparatuses using the above first and second chemical  
25 treatment methods, i.e., various apparatuses using the  
cathode electrolysis reduction treatment and acid dip  
treatment according to the first chemical treatment



method, and various apparatuses using the acid electrolysis treatment according to the second chemical treatment method.

[Application Example 1] to [Application Example 4] relate to an apparatus for etching a metal film formed on a carrier tape. [Application Example 5] and [Application Example 6] relate to an apparatus for etching a metal film formed on a semiconductor wafer. Assume that, as shown in FIG. 2E, a chromium film 120 is formed on the carrier tape or semiconductor wafer, and a copper film 130 and resist film 140 are etched into a predetermined pattern in this order on the chromium film 120.

[Application Example 1]

Application Example 1 relates to an example of "a vertical feed type" apparatus which uses the first chemical treatment method described above, and in which a carrier tape is fed as it is set upright, i.e., fed such that the tape widthwise direction is vertical. FIG. 5 is a schematic side sectional view showing an example of the vertical feed type chemical treatment apparatus. FIG. 6 is a schematic front sectional view of a cathode electrolysis reduction device forming the chemical treatment apparatus shown in FIG. 5.

As shown in FIG. 5, a chemical treatment apparatus 30 comprises a cathode electrolysis reduction device 31 for performing a cathode electrolysis reduction

treatment for a carrier tape C1, washing devices 32 and 34 for washing the carrier tape C1, and an acid dip device 33 for performing an acid dip treatment for the carrier tape C1.

5           A feeding device (not shown) for feeding the carrier tape C1 is placed at the left end of the cathode electrolysis reduction device 31 in FIG. 5. Also, a winding device (not shown) for winding up the carrier tape C1 is placed at the right end of the  
10           washing device 34.

          As shown in FIGS. 5 and 6, the cathode electrolysis reduction device 31 has a box-like external treatment bath 31a. An internal treatment bath 31b is formed in a substantially central portion  
15           of the external treatment bath 31a. The bottom of the external treatment bath 31a also functions as the bottom of the internal treatment bath 31b. The side walls of the internal treatment bath 31b are slightly lower than the side walls of the external treatment  
20           bath 31a.

          One end of a supply pipe 31c is connected to the bottom of the internal treatment bath 31b. A pump 31d, heat exchanger 31e, and filter 31f are arranged midway along the supply pipe 31c. The other end of the supply  
25           pipe 31c is connected to a tank 31g. The tank 31g contains a treatment solution 31h. The treatment solution 31h is one of an acidic treatment solution

containing an acid radical and an alkaline treatment solution containing halogen ion. Preferably, the treatment solution 31h is a chloride-ion-containing treatment solution such as SAS manufactured by K.K.

5 MURATA. One end of each of drain pipes 31i and 31j is connected to a bottom portion between the external treatment bath 31a and the internal treatment bath 31b. The other ends of the drain pipes 31i and 31j are connected to the tank 31g.

10           When the pump 31d is operated, the treatment solution 31h in the tank 31g flows through the supply pipe 31c via the heat exchanger 31e and filter 31f, and is supplied to the internal treatment bath 31b. When a predetermined amount of the treatment solution 31h is  
15 supplied to the internal treatment bath 31b, the treatment solution 31h flows outside the internal treatment bath 31b over its side walls. That is, the treatment solution 31h overflows from the internal treatment bath 31b into an overflow portion 31k formed  
20 between the side walls of the external treatment bath 31a and the side walls of the internal treatment bath 31b. The treatment solution 31h flowing into the overflow portion 31k is collected to the tank 31g through the drain pipes 31i and 31j. After that, the  
25 treatment solution 31h repetitively circulates through the individual members as described above.

As shown in FIGS. 5 and 6, of the side walls of

the external treatment bath 31a and internal treatment bath 31b, slits 31l and 31m as long vertical holes are formed in predetermined portions of side walls through which the carrier tape C1 passes. Each of the slits  
5 31l and 31m has a width and length larger than those of the carrier tape C1. Note that the treatment solution 31h in the internal treatment bath 31b also flows out into the overflow portion 31k through the slits 31m.

An electrode 31n is placed inside the internal  
10 treatment bath 31b. In the internal treatment bath 31b, the electrode 31n faces one surface, i.e., a surface on which films are formed, of the carrier tape C1. The electrode 31n is connected to the positive pole of a power supply 31x.

15 Of the side walls of the external treatment bath 31a, electrode rollers 31y and 31z are arranged outside a side wall through which the carrier tape C1 is loaded, and a side wall through which the carrier tape C1 is unloaded. The electrode rollers 31y and 31z are  
20 in contact with one surface, i.e., a surface on which a chromium film and copper film are formed, of the carrier tape C1. The electrode rollers 31y and 31z are connected to the negative pole of the power supply 31x.

The washing devices 32 and 34 and acid dip device  
25 33 have substantially the same arrangement as the cathode electrolysis reduction device 31.

The washing device 32 has a box-like external

treatment bath 32a, and an internal treatment bath 32b is formed in a substantially central portion of the external treatment bath 32a. A supply pipe 32c is connected to the bottom of the internal treatment bath 32b. Drain pipes 32i and 32j are connected to the bottom of the external treatment bath 32a. A tank 32g contains deionized water 32h for washing the carrier tape C1.

When a pump 32d is operated, the deionized water 32h in the tank 32g flows through the supply pipe 32c via a heat exchanger 32e and filter 32f, and is supplied to the internal treatment bath 32b. After that, the deionized water 32h in the tank 32g flows into an overflow portion 32k over the side walls of the internal treatment bath 32b. The deionized water 32h is collected to the tank 32g through the drain pipes 32i and 32j, and circulates in the same manner as above.

Of the side walls of the external treatment bath 32a and internal treatment bath 32b, slits 32l and 32m are formed in predetermined portions of side walls through which the carrier tape C1 passes. The carrier tape C1 is fed as it passes through the slits 32l and 32m and is dipped in the deionized water 32h in the internal treatment bath 32b.

The acid dip device 33 has a box-like external treatment bath 33a, and an internal treatment bath 33b

is formed in a substantially central portion of the external treatment bath 33a. A supply pipe 33c is connected to the bottom of the internal treatment bath 33b. Drain pipes 33i and 33j are connected to the bottom of the external treatment bath 33a. A tank 33g contains a treatment solution 33h. The treatment solution 33h is an acidic treatment solution, preferably, an acidic treatment solution containing halogen ion, such as SAS manufactured by K.K. MURATA.

When a pump 33d is operated, the treatment solution 33h in the tank 33g flows through the supply pipe 33c via a heat exchanger 33e and filter 33f, and is supplied to the internal treatment bath 33b. After that, the treatment solution 33h in the tank 33g flows into an overflow portion 33k over the side walls of the internal treatment bath 33b. The treatment solution 33h is collected to the tank 33g through the drain pipes 33i and 33j, and circulates in the same manner as above.

Of the side walls of the external treatment bath 33a and internal treatment bath 33b, slits 33l and 33m are formed in predetermined portions of side walls through which the carrier tape C1 passes. The carrier tape C1 is fed as it passes through the slits 33l and 33m and is dipped in the treatment solution 33h in the internal treatment bath 33b.

The washing device 34 has a box-like external

treatment bath 34a, and an internal treatment bath 34b is formed in a substantially central portion of the external treatment bath 34a. A supply pipe 34c is connected to the bottom of the internal treatment  
5 bath 34b. Drain pipes 34i and 34j are connected to the bottom of the external treatment bath 34a. A tank 34g contains deionized water 34h for washing the carrier tape C1.

When a pump 34d is operated, the deionized water  
10 34h in the tank 34g flows through the supply pipe 34c via a heat exchanger 34e and filter 34f, and is supplied to the internal treatment bath 34b. After that, the deionized water 34h in the tank 34g flows into an overflow portion 34k over the side walls of the  
15 internal treatment bath 34b. The deionized water 34h is collected to the tank 34g through the drain pipes 34i and 34j, and circulates in the same manner as above.

Of the side walls of the external treatment bath  
20 34a and internal treatment bath 34b, slits 34l and 34m are formed in predetermined portions of side walls through which the carrier tape C1 passes. The carrier tape C1 is fed as it passes through the slits 34l and 34m and is dipped in the deionized water 34h in the  
25 internal treatment bath 34b.

Feed rollers (not shown) are arranged on the two sides of each of the devices 31 to 34. These feed

rollers sandwich the carrier tape C1 between them and rotate adjacent to each other in opposite directions. The carrier tape C1 is fed when these feed rollers rotate. As described above, the electrode rollers 31y and 31z are arranged on the two sides of the cathode electrolysis reduction device 31. Feed rollers are arranged opposite to the electrode rollers 31y and 31z with the carrier tape C1 interposed between them.

5 The operation of the chemical treatment apparatus 30 will be explained below.

When the electrode rollers 31y and 31z and the feed rollers rotate in predetermined directions, the carrier tape C1 is fed in the feed direction from the feeding device (not shown). Accordingly, the carrier tape C1 passes through the internal treatment baths 31b to 34b of the devices 31 to 34, and is wound up by the winding device (not shown).

15 The following treatments are performed in the devices 31 to 34.

20 That is, in the cathode electrolysis reduction device 31, the internal treatment bath 31b is filled with the treatment solution 31h, and a voltage is applied between the electrode rollers 31y and 31z and the electrode 31n. In this state, the carrier tape C1 passes through the slits 31l and 31m and through the internal treatment bath 31b. When passing through the internal treatment bath 31b, the carrier tape C1 is



subjected to the cathode electrolysis reduction treatment. That is, outside the external treatment bath 31a, the electrode rollers 31y and 31z are in contact with the surface of the carrier tape C1 on which the metal films are formed. Therefore, in the internal treatment bath 31b, a chromium oxide film formed on the surface of the chromium film is reduced.

In the washing device 32, the internal treatment bath 32b is filled with the deionized water 32h. The carrier tape C1 passes through the slits 32l and 32m, and is washed with the deionized water 32h when passing through the internal treatment bath 32b.

In the acid dip device 33, the internal treatment bath 33b is filled with the treatment solution 33h. The carrier tape C1 passes through the slits 33l and 33m, and is subjected to the acid dip treatment in the internal treatment bath 33b. That is, the carrier tape C1 is fed as it is dipped in the treatment solution 33h in the internal treatment bath 33b, and the chromium film formed on the carrier tape C1 is etched into a predetermined pattern.

In the washing device 34, the internal treatment bath 34b is filled with the deionized water 34h. The carrier tape C1 passes through the slits 34l and 34m, and is washed with the deionized water 34h when passing through the internal treatment bath 34b. The carrier tape C1 washed by the washing device 34 is

dried through a drying device (not shown) and wound up by the winding device (not shown).

By the above operation, the chromium film formed on the carrier tape C1 can be etched into a predetermined pattern. Also, the production of hexavalent chromium can be prevented.

As shown in FIGS. 5 and 6, in the cathode electrolysis reduction treatment in the cathode electrolysis reduction device 31, it is possible to completely fill the internal treatment bath 31b with the treatment solution 31h, and entirely dip the carrier tape C1 in the treatment solution 31h. It is also possible to fill the internal treatment bath 31b not completely with the treatment solution 31h, and dip in the treatment solution 31h a portion of the surface of the carrier tape C1 on which the metal film is formed.

[Application Example 2]

Application Example 2 uses an apparatus which uses the second chemical treatment method described above, and which is a vertical feed type chemical treatment apparatus similar to that of Application Example 1. FIG. 7 is a schematic sectional view showing an example of the chemical treatment apparatus. As shown in FIG. 7, a chemical treatment apparatus 40 comprises an electrolysis device 41 for performing an acid electrolysis treatment for a carrier tape C2, and

a washing device 42 for washing the carrier tape C2.

In the chemical treatment apparatus 40, similar to the chemical treatment apparatus 30 shown in FIG. 5, a feeding device and winding device (neither is shown) are arranged at the two ends of the electrolysis device 41 and washing device 42.

The electrolysis device 41 has substantially the same arrangement as the cathode electrolysis reduction device 31 shown in FIGS. 5 and 6. In the electrolysis device 41, however, an electrode roller 41y is placed on the feeding device side of an external treatment bath 41l. The electrolysis device 41 also differs from the cathode electrolysis reduction device 31 in that a tank 41g contains an acidic treatment solution, preferably, an acidic treatment solution 41h containing halogen ion such as chloride ion. A preferred example of the acidic treatment solution 41h is SAS manufactured by K.K. MURATA.

The washing device 42 has substantially the same arrangement as the washing devices 32 and 34 shown in FIG. 5. In the washing device 42, therefore, deionized water 42h in a tank 42g flows through a supply pipe 42c and internal treatment bath 42b via a heat exchanger 42e and filter 42f by an operation of a pump 42d.

The deionized water 42h circulates from an overflow portion 42k to drain pipes 42i and 42j.

The operation of the chemical treatment apparatus

40 will be explained below.

When the electrode roller 41y and feed rollers rotate in predetermined directions, the carrier tape C2 is wound up through the internal treatment baths 41b and 42b in the electrolysis device 41 and washing device 42, respectively.

The following treatments are performed in the devices 41 and 42.

In the electrolysis device 41, the internal treatment bath 41b is filled with the treatment solution 41h. The treatment solution 41h overflowing from the internal treatment bath 41b is collected from the overflow portion 41k to the tank 41g through the drain pipes 41i and 41j. By the operation of the pump 41d, the treatment solution 41h flows from the tank 41g to the supply pipe 41c via a heat exchanger 41e and filter 41f, and circulates to the internal treatment bath 41b. Also, in the electrolysis device 41, a power supply 41x applies a voltage between the electrode roller 41y and an electrode 41n.

In this state, the carrier tape C2 passes through slits 41l and 41m and through the internal treatment bath 41b. When passing through the internal treatment bath 41b, the carrier tape C2 is subjected to an acid electrolysis treatment. That is, outside the external treatment bath 41a, the electrode roller 41y is in contact with the surface of the carrier tape C2 on

which a metal film is formed. Therefore, when the carrier tape C2 opposes the electrode 41n, a chromium oxide film formed on the surface of a chromium film is reduced. After that, when a region of the reduced chromium film comes off a region facing the electrode 41n as the carrier tape C2 is fed, the chromium film on the carrier tape C2 is etched into a predetermined pattern by the treatment solution 41h in the internal treatment bath 41b.

In the washing device 42, the internal treatment bath 42b inside an external treatment bath 42a is filled with the deionized water 42h. The carrier tape C2 passes through slits 42l and 42m, and is washed with the deionized water 42h when passing through the internal treatment bath 42b. The carrier tape C2 washed by the washing device 42 is dried through a drying device (not shown), and wound up by the winding device (not shown).

By the above operation, the chromium film formed on the carrier tape C2 can be etched into a predetermined pattern. Also, the production of hexavalent chromium can be prevented.

[Application Example 3]

Application Example 3 relates to an example of "a horizontal feed type" apparatus which uses the first chemical treatment method described above, and in which a carrier tape is fed as it is horizontally laid down.

FIG. 8 is a schematic side sectional view showing an example of the horizontal feed type chemical treatment apparatus.

As shown in FIG. 8, a chemical treatment apparatus 50 comprises a cathode electrolysis reduction device 51 for performing a cathode electrolysis reduction treatment for a carrier tape C3, washing devices 52 and 54 for washing the carrier tape C3, and an acid dip device 53 for performing an acid dip treatment for the carrier tape C3.

In the chemical treatment apparatus 50, similar to the chemical treatment apparatuses 30 and 40 shown in FIGS. 5 to 7, a feeding device (not shown) for feeding the carrier tape C3 is placed at the left end of the cathode electrolysis reduction device 51 in FIG. 8, and a winding device (not shown) for winding up the carrier tape C3 is placed at the right end of the washing device 54 in FIG. 8.

The cathode electrolysis reduction device 51 has a treatment bath 51a which contains a treatment solution 51b. The treatment solution 51b is one of an acidic treatment solution containing an acid radical and an alkaline treatment solution containing halogen ion. Preferably, the treatment solution 51b is a chloride-ion-containing treatment solution such as SAS manufactured by K.K. MURATA. The two ends of a flow pipe 51c are connected to the bottom of the

treatment bath 51a. A pump 51d, heat exchanger 51e, and filter 51f are arranged midway along the flow pipe 51c. When the pump 51d is operated, the treatment solution 51b in the treatment bath 51a flows through  
5 the flow pipe 51c and returns to the treatment bath 51a via the heat exchanger 51e and filter 51f. In the cathode electrolysis reduction device 51, such a circulating system of the treatment solution 51b is formed.

10 Two electrode rollers 51g and 51h are arranged above the treatment bath 51a, and connected to the negative pole of a power supply 51i. Backup rollers 51j and 51k for supporting the electrode rollers 51g and 51h are arranged below the electrode rollers 51g  
15 and 51h, respectively. In the treatment bath 51a, a feed roller 51l for changing the feeding direction of the carrier tape C3 is placed.

The carrier tape C3 is sandwiched between the electrode roller 51g and the backup roller 51j, wound  
20 around the feed roller 51l in the treatment bath 51a, and sandwiched between the electrode roller 51h and the backup roller 51k. The surface of the carrier tape C3 on which a metal film is formed is in contact with the electrode rollers 51g and 51h.

25 In the treatment bath 51a, two electrodes 51m and 51n are arranged. The electrodes 51m and 51n are connected to the positive pole of the power supply 51i,

and oppose the carrier tape C3. Note that in the treatment bath 51a, the electrodes 51m and 51n oppose the surface of the carrier tape C3 on which a metal film is formed.

5           The washing device 52 has a treatment bath 52a which contains deionized water 52b. The two ends of a flow pipe 52c are connected to the bottom of the treatment bath 52a. A pump 52d, heat exchanger 52e, and filter 52f are arranged midway along the flow  
10       pipe 52c. When the pump 52d is operated, the deionized water 52b in the treatment bath 52a flows through the flow pipe 52c and returns to the treatment bath 52a via the heat exchanger 52e and filter 52f. In the washing device 52, such a circulating system of the deionized  
15       water 52b is formed.

          Four feed rollers 52g, 52h, 52i, and 52j are arranged above the treatment bath 52a. That is, the feed rollers 52g and 52h make a pair on the upstream side in the feeding direction of the carrier tape C3,  
20       and the feed rollers 52i and 52j make a pair on the downstream side. In the treatment bath 52a, a feed roller 52l for changing the feeding direction of the carrier tape C3 is placed.

          The carrier tape C3 is sandwiched between the feed  
25       rollers 52g and 52h, and wound around the feed roller 52l in the treatment bath 52a. In the washing device 52, such a feeding system of the carrier tape C3 is



formed.

The acid dip device 53 has a treatment bath 53a which contains a treatment solution 53b. The treatment solution 53b is an acidic treatment solution, preferably, an acidic treatment solution containing halogen ion such as chloride ion. An example of this acidic treatment solution is SAS manufactured by K.K. MURATA. The two ends of a flow pipe 53c are connected to the bottom of the treatment bath 53a. A pump 53d, heat exchanger 53e, and filter 53f are arranged midway along the flow pipe 53c. When the pump 53d is operated, the treatment solution 53b in the treatment bath 53a flows through the flow pipe 53c and returns to the treatment bath 53a via the heat exchanger 53e and filter 53f. In the acid dip device 53, such a circulating system of the treatment solution 53b is formed.

Four feed rollers 53g, 53h, 53i, and 53j are arranged above the treatment bath 53a. That is, the feed rollers 53g and 53h make a pair on the upstream side in the feeding direction of the carrier tape C3, and the feed rollers 53i and 53j make a pair on the downstream side. In the treatment bath 53a, a feed roller 53l for changing the feeding direction of the carrier tape C3 is placed.

The carrier tape C3 is sandwiched between the feed rollers 53g and 53h, wound around the feed roller 53l

in the treatment bath 53a, and sandwiched between the feed rollers 53i and 53j.

5 The washing device 54 has the same arrangement as the washing device 52. That is, a treatment bath 54a contains deionized water 54b. A circulating system made up of a flow pipe 54c, a pump 54d, a heat exchanger 54e, a filter 54f, and the treatment bath 54a has the same arrangement as that of the washing device 52. Also, a feeding system made up of four feed  
10 rollers 54g, 54h, 54i, and 54j above the treatment bath 54a and a feed roller 54l in the treatment bath 54a has the same arrangement as that of the washing device 52.

In the treatment baths 51a, 52a, 53a, and 54a of the devices 51, 52, 53, and 54, the solutions 51b, 52b,  
15 53b, and 54b are agitated by agitators (not shown) or the like.

The operation of the chemical treatment apparatus 50 will be explained below.

When the feed rollers including the electrode  
20 rollers 51g and 51h rotate in predetermined directions, the carrier tape C3 is fed in the feeding direction from the feeding device, and wound up by the winding device through the treatment baths 51a to 54a of the devices 51 to 54. As shown in FIG. 8, the carrier tape  
25 C3 is fed zigzag when viewed sideways.

The following treatments are performed in the devices 51 to 54.

In the cathode electrolysis reduction apparatus 51, the treatment bath 51a is filled with the treatment solution 51b, and a voltage is applied between the electrode rollers 51g and 51h and the electrodes 51m and 51n. In this state, the carrier tape C3 is subjected to a cathode electrolysis reduction treatment when passing through the treatment bath 51a. That is, outside the treatment bath 51a, the electrode rollers 51g and 51h are in contact with the surface of the carrier tape C3 on which a metal film is formed. Therefore, a chromium oxide film formed on the surface of a chromium film is reduced under the influence of the electrodes 51m and 51n.

In the washing device 52, the treatment bath 52a is filled with the deionized water 52b, and the carrier tape C3 is washed with the deionized water 52b when passing through the treatment bath 52a.

In the acid dip device 53, the treatment bath 53a is filled with the treatment solution 53b, and the carrier tape C3 is subjected to an acid dip treatment when passing through the treatment bath 53a. That is, the carrier tape C3 is fed as it is dipped in the treatment solution 53b in the treatment bath 53a, and the chromium film is etched into a predetermined pattern.

In the washing device 54, the treatment bath 54a is filled with the deionized water 54b, and the carrier

tape C3 is washed with the deionized water 54b when passing through the treatment bath 54a. The carrier tape C3 washed by the washing device 54 is dried by a drying device (not shown), and wound up by the winding device (not shown).

By the above operation, the chromium film formed on the carrier tape C3 can be etched into a predetermined pattern. Also, the production of hexavalent chromium can be prevented.

[Application Example 4]

Application Example 4 uses an apparatus which uses the second chemical treatment method described above, and which is a horizontal feed type chemical treatment apparatus similar to that of Application Example 3.

FIG. 9 is a schematic side sectional view showing an example of this chemical treatment apparatus. As shown in FIG. 9, a chemical treatment apparatus 60 comprises an electrolysis device 61 for performing an acid electrolysis treatment for a carrier tape C4, and a washing device 62 for washing the carrier tape C4.

In the chemical treatment apparatus 60, similar to the chemical treatment apparatus 50 shown in FIG. 8, a feeding device and winding device (neither is shown) are arranged at the two ends of the electrolysis device 61 and washing device 62 shown in FIG. 9.

The electrolysis device 61 has a treatment bath 61a which contains a treatment solution 61b.

The treatment solution 61b is a halogen-ion-containing acidic treatment solution, preferably, a chloride-ion-containing treatment solution such as SAS manufactured by K.K. MURATA. The electrolysis device 61 has a circulating system similar to that of the cathode electrolysis reduction device 51 shown in FIG. 8. That is, the treatment solution 61b circulates between individual members by a circulating system made up of a supply pipe 61c, a pump 61d, a heat exchanger 61e, a filter 61f, and the treatment bath 61a.

An electrode roller 61g is placed above the treatment bath 61a and connected to the negative pole of a power supply 61i. A backup roller 61h for supporting the electrode roller 61g is placed below the electrode roller 61g. The electrode roller 61g and backup roller 61h are arranged on the upstream side in the feeding direction of the carrier tape C4. Two feed rollers 61j and 61k adjacent to each other are arranged on the downstream side in the feeding direction of the carrier tape C4. In the treatment bath 61a, a feed roller 61l for changing the feeding direction of the carrier tape C4 is placed.

The carrier tape C4 is sandwiched between the electrode roller 61g and the backup roller 61h, wound around the feed roller 61l in the treatment bath 61a, and sandwiched between the electrode roller 61j and the feed roller 61k. The surface of the carrier tape C4 on

which a metal film is formed is in contact with the electrode roller 61g.

5 An electrode 61m is placed in the treatment bath 61a, and connected to the positive pole of the power supply 61i. Note that in the treatment bath 61a, the electrode 61m opposes the surface of the carrier tape C4 on which a metal film is formed, before the carrier tape C4 reaches the feed roller 61l.

10 The washing device 62 has the same arrangement as the washing device 52 shown in FIG. 8. That is, a treatment bath 62a contains deionized water 62b. A circulating system made up of a flow pipe 62c, a pump 62d, a heat exchanger 62e, a filter 62f, and the treatment bath 62a, and a feeding system made up of  
15 four feed rollers 62g, 62h, 62i, and 62j above the treatment bath 62a and a feed roller 62l inside the treatment bath 62a have the same arrangements as those of the washing device 52 described earlier.

20 The operation of the chemical treatment apparatus 60 will be explained below.

When the feed rollers including the electrode roller 61g rotate in predetermined directions, the carrier tape C4 is fed in the feeding direction from the feeding device, and wound up by the winding device  
25 through the treatment baths 61a and 62a of the devices 61 and 62. As shown in FIG. 9, the carrier tape C4 is fed zigzag when viewed sideways.

The following treatments are performed in the devices 61 and 62.

5 In the electrolysis apparatus 61, the treatment bath 61a is filled with the treatment solution 61b, and a voltage is applied between the electrode rollers 61g and the electrode 61m. In this state, the carrier tape C4 is subjected to an acid electrolysis treatment when passing through the treatment bath 61a.

10 That is, outside the treatment bath 61a, the electrode roller 61g is in contact with the surface of the carrier tape C4 on which a metal film is formed. Therefore, when opposing the electrode 61m, a chromium oxide film formed on the surface of a chromium film is reduced under the influence of the electrode 61m.  
15 After that, the reduced chromium film is fed by the feed roller 61l. Since the chromium film is dipped in the treatment solution 61b, this chromium film is etched into a predetermined pattern by the treatment solution 61b.

20 In the washing device 62, the treatment bath 62a is filled with the deionized water 62b, and the carrier tape C4 is washed with the deionized water 62b when passing through the treatment bath 62a. The carrier tape C4 washed by the washing device 62 is dried by  
25 a drying device (not shown), and wound up by the winding device (not shown).

By the above operation, the chromium film

formed on the carrier tape C4 can be etched into a predetermined pattern. Also, the production of hexavalent chromium can be prevented.

[Application Example 1] to [Application Example 4] disclose treatments for the carrier tapes C1, C2, C3, and C4 each having a metal film formed on one surface. However, a carrier tape having metal films on the two surfaces can also be treated in the same manner as above. In this case, electrodes are opposed to both the surfaces of the carrier tape in a treatment bath filled with a treatment solution, and are connected to the positive pole of a power supply.

In the cathode electrolysis reduction device 31 of [Application Example 1], a cathode electrolysis reduction treatment is performed with the internal treatment bath 31b filled with the treatment solution 31h. However, instead of this arrangement, it is also possible to install in the internal treatment bath 31b a shower nozzle communicating with the supply pipe 31c such that this shower nozzle faces the surface of the carrier tape C1 on which a metal film is formed, and gush the treatment solution 31h against the carrier tape C1 from the shower nozzle.

Similar to the cathode electrolysis reduction device 31, it is also possible in the acid dip device 33 to install a shower nozzle in the internal treatment bath 33b and gush the treatment solution 33h against



the carrier tape C1 from the shower nozzle.

5 If metal films are formed on the two surfaces of the carrier tape C1, shower nozzles are installed in the internal treatment baths 31b and 33b of the cathode electrolysis reduction device 31 and acid dip device 33 so as to face the two surfaces of the carrier tape C1, and the treatment solutions 31h and 33h are gushed against the carrier tape C1 from these shower nozzles.

10 Furthermore, in the cathode electrolysis reduction device 51 of [Application Example 3], a cathode electrolysis reduction treatment is performed with the internal treatment bath 51a filled with the treatment solution 51b. However, instead of this arrangement, it is also possible to install in the internal treatment bath 51a a shower nozzle communicating with the supply pipe 51c such that this shower nozzle faces the surface of the carrier tape C3 on which a metal film is formed, and gush the treatment solution 51b against the carrier tape C3 from the shower nozzle.

20 Similar to the cathode electrolysis reduction device 51, it is also possible in the acid dip device 53 to install a shower nozzle in the treatment bath 53a and gush the treatment solution 53b against the carrier tape C3 from the shower nozzle.

25 If metal films are formed on the two surfaces of the carrier tape C3, shower nozzles are installed in the treatment baths 51a and 53a of the cathode

electrolysis reduction device 51 and acid dip device 53 so as to face the two surfaces of the carrier tape C3, and the treatment solutions 51b and 53b are gushed against the carrier tape C3 from these shower nozzles.

5 [Application Example 5]

Application Example 5 relates to a chemical treatment apparatus which uses the first chemical treatment method described above, and which is used when a metal film formed on a semiconductor wafer is  
10 etched into a predetermined pattern. This chemical treatment apparatus comprises a cathode electrolysis reduction device for performing a cathode electrolysis reduction treatment for a metal film on a semiconductor wafer, and an acid dip device for performing an acid  
15 dip treatment for the metal film on the semiconductor wafer after the cathode electrolysis reduction treatment.

First, the cathode electrolysis reduction device will be explained below.

20 FIG. 10 is a longitudinal side sectional view showing an example of a cathode electrolysis reduction device 71. As shown in FIG. 10, a cup 2 is placed on a support table 1. The lower portion of the cup 2 is open, and the cup 2 is mounted on the support table 1 with this open surface facing down. The support  
25 table 1 is vertically movable, and the cup 2 is fixed to the device main body. Accordingly, the support

table 1 moves up and down with the cup 2 fixed to the device main body.

5 A suction path 3 is formed in the support table 1. The suction path 3 is connected to a suction means such as a vacuum pump (not shown) through a duct 3a below the suction path 3. In the upper portion of the support table 1, a large number of suction holes 3b which open upward are formed. The surface surrounding the suction holes 3b inclines outward from above, thereby forming an inclined engaging surface 1a on the support table 1. When the cup 2 is to be united, the inclined engaging surface 1a engages with an inclined engaging surface 9b of a guide ring 9 (to be described later), thereby effectively aligning the support table 1 with the cup 2.

15 A mesh-like anode electrode 4 is formed in the upper portion of the interior of the cup 2. The anode electrode 4 is connected to an anode 5 of a power supply 19. In the lower portion of the cup 2, an annular-plate-like closing sheet 6 made of elastic viton rubber is so formed as to surround the open surface of the cup 2. On the lower surface of the closing sheet 6, three plate-like cathode electrodes 7 are formed. The cathode electrodes 7 are equally spaced, i.e., separated at a central angle of  $120^\circ$ , and connected to a cathode 8 of the power supply 19.

20 The guide ring 9 is overlapped on and integrated

with the lower side of the closing sheet 6. In the lower portion of the cup 2, aligning projections 2a are formed in three portions equally spaced, i.e., separated at a central angle of 120°. In one-to-one  
5 correspondence with the aligning projections 2a, aligning through holes 6a are formed in the closing sheet 6, aligning through holes 7a are formed in the cathode electrodes 7, and aligning recesses 9a are formed in the upper portion of the guide ring 9.

10 The aligning projections 2a extend through the aligning through holes 6a and 7a and engage with the aligning recesses 9a, thereby fixing the closing sheet 6 and cathodes 7 to the cup 2. The inclined engaging surface 9b which inclines outward from above is formed  
15 on the inner circumference of the guide ring 9. The inclined engaging surface 9b engages with the inclined engaging surface 1a of the support table 1.

When the cup 2, closing sheet 6, cathode electrodes 7, and guide ring 9 as described above are  
20 integrated, the cathode electrodes 7 are exposed by about 3 to 4 mm inside the guide ring 9, and the rest is completely covered with the closing sheet 6 and guide ring 9. Accordingly, only the end portion of each cathode electrode 7 is in contact with a treatment  
25 solution 12, and the rest is not in contact with the treatment solution 12 at all. An O-ring 10 is interposed between the lower surface of the guide ring

9 and the support table 1.

A semiconductor wafer W1 is supported on the support table 1 while the edge of the semiconductor wafer W1 is clamped between the closing sheet 6 and the support table 1. In addition, the semiconductor wafer W1 is connected to the end portion of each cathode electrode 7 via a connecting terminal (not shown).

The tank 13 contains the treatment solution 12 which flows into the cup 2. The treatment solution 12 is one of an acidic treatment solution containing an acid radical and an alkaline treatment solution containing halogen ion. Preferably, the treatment solution 12 is a chloride-ion-containing treatment solution such as SAS manufactured by K.K. MURATA. A pump 14 for pumping up the treatment solution 12 in the tank 13 is positioned above the tank 13. A supply path 15 is formed between the pump 14 and the lower portion of the cup 2. The treatment solution 12 pumped up from the tank 13 by the pump 14 flows into the cup 2 through the supply path 15.

A drain path 16 is formed in a substantially central portion of the upper portion of the cup 2. Outside the cup 2, a relief valve 17 is connected to the drain path 16. A return path 18 is branched from a passage between the drain path 16 and the relief valve 17, and connected to the tank 13.

The acid dip device will be described next.

FIG. 11 is a longitudinal side sectional view showing an example of an acid dip device 72. As shown in FIG. 11, a cup 82 is formed on a support table 81. The lower portion of the cup 82 is open, and the cup 82 is mounted on the support table 81 with this open surface facing down. In the lower portion of the cup 82, an annular-plate-like closing sheet 6 (not shown) made of elastic viton rubber is so formed as to surround the open surface of the cup 82. The support table 81 is vertically movable, and the cup 82 is fixed to the device main body. Accordingly, the support table 81 moves up and down with the cup 82 fixed to the device main body.

A suction path 83 is formed in the support table 81. The suction path 83 is connected to a suction means such as a vacuum pump (not shown) through a duct 83a below the suction path 83. In the upper portion of the support table 81, a large number of suction holes 83b which open upward are formed. All the suction holes 83b are covered with the cup 82. An O-ring 84 is interposed between the lower portion of the cup 82 and the support table 81.

A semiconductor wafer W1 is clamped between the lower portion of the cup 82 and the support table 81.

A tank 85 is positioned below the cup 82. The tank 85 contains a treatment solution 86 which flows into the cup 82. The treatment solution 86 is

an acidic treatment solution, e.g., an acidic treatment solution containing halogen ion, preferably, chloride ion. A preferred example of this acidic treatment solution is SAS manufactured by K.K. MURATA. A pump 87  
5 for pumping up the treatment solution 86 from the tank 85 is positioned above the tank 85. A supply path 88 is formed between the pump 87 and the cup 82. The treatment solution 86 pumped up from the tank 85 by the pump 87 flows into the cup 82 through the supply  
10 path 88.

A drain path 89 is formed in a substantially central portion of the upper portion of the cup 82. Outside the cup 82, a relief valve 90 is connected to the drain path 89. A return path 91 is branched from  
15 a passage between the drain path 89 and the relief valve 90, and connected to the tank 85.

The operations of the cathode electrolysis reduction device 71 and acid dip device 72 shown in FIGS. 10 and 11 will be explained below.

20 First, in the cathode electrolysis reduction device 71, the support table 1 and cup 2 are separated by moving down the support table 1 from the cup 2. After that, a semiconductor wafer W1 is set on the support surface of the support table 1 such that  
25 a metal film formed on the semiconductor wafer W1 faces up. The suction means connected to the duct 3a is operated to exert suction force on the suction holes

3b, thereby fixing the semiconductor wafer W1 on the support table 1 by suction.

Subsequently, while the semiconductor wafer W1 is thus fixed, the support table 1 providing O-ring 10 is moved up to engage the inclined engaging surface 1a of the support table 1 with the inclined engaging surface 9b of the guide ring 9, thereby aligning the support table 1 with the cup 2. In this manner, the interior of the cup 2 is completely closed by the lower surface of the clothing sheet 6 and the O-ring 10. In this state, the edge of the semiconductor wafer W1 is in tight contact with the lower surface of the closing sheet 6, and the metal film on the semiconductor wafer W1 is connected to the cathode electrodes 7.

After that, the pump 14 is driven to supply the treatment solution 12 from the tank 13 into the cup 2 through the supply path 15. Consequently, the treatment solution 12 flows into the cup 2 from above the semiconductor wafer W1, and builds up in the cup 2 with time. In this stage, the relief valve 17 is still closed, and the air in the cup 2 is exhausted into the tank 13 and then to the outside through the drain path 16 and return path 18, so no air remains in the piping system. Similar to the internal air of the cup 2, a gas produced on the surface of the semiconductor wafer W1 is also exhausted outside.

When the anode electrode 4 is well dipped in



the treatment solution 12 flowing into the cup 2 and the treatment solution 12 reaches the return path 18 through the drain path 16, a cathode electrolysis reduction treatment is performed for the semiconductor wafer W1. That is, an electric current is supplied between the anode electrode 4 and each cathode electrode 7 for a predetermined time by the power supply 19, thereby turning a chromium film on the semiconductor wafer W1 into a cathode. Consequently, the chromium film is subjected to electrolysis reduction in the treatment solution 12, so a chromium oxide film formed on the surface of the chromium film is reduced.

After the electric current is supplied for the predetermined time to complete the cathode electrolysis reduction treatment, the relief valve 17 is opened to expose the drain path 16 and return path 18 to the atmosphere. As a consequence, the treatment solution 12 in the return path 18 is collected to the tank 13 through the return path 18. Since the tank 13 is positioned below the cup 2, the treatment solution 12 in the cup 2 is also collected to the tank 13 through the supply path 15 and pump 14. After that, the support table 1 is moved down to release the semiconductor wafer W1 from fixation to the support surface by suction. In this way, the cathode electrolysis reduction treatment by the cathode

electrolysis reduction device 71 is complete.

After that, the semiconductor wafer W1 is transferred to a washing device (not shown) by a transfer means (not shown) such as a transfer robot, and washed by the washing device. When the washing treatment is complete, the semiconductor wafer W1 is transferred the acid dip device 72 shown in FIG. 11.

In the acid dip device 72, the support table 81 and cup 82 are separated by moving down the support table 81 from the cup 82. The semiconductor wafer W1 is set on the support surface of the support table 81 such that the metal film of the semiconductor wafer W1 faces up. The suction means connected to the duct 83a is operated to exert suction force on the suction holes 83b, thereby fixing the semiconductor wafer W1 on the support table 81 by suction.

Subsequently, while the semiconductor wafer W1 is thus fixed, the support table 81 providing O-ring 84 is moved up to align the support table 81 with the cup 82. In this manner, the interior of the cup 82 is completely closed.

After that, the pump 87 is driven to supply the treatment solution 86 from the tank 85 into the cup 82 through the supply path 88. Consequently, the treatment solution 86 flows into the cup 82 from above the semiconductor wafer W1, and builds up in the cup 82 with time. In this stage, the relief valve 90 is still

closed, and the air in the cup 82 is exhausted into the tank 85 and then to the outside through the drain path 89 and return path 91, so no air remains in the piping system. Similar to the internal air of the cup 82, a  
5 gas produced on the surface of the semiconductor wafer W1 is also exhausted outside.

When a predetermined amount of the treatment solution 86 builds up in the cup 82, supply of the treatment solution 86 from the tank 85 is stopped,  
10 and an acid dip treatment is performed for the semiconductor wafer W1. That is, the semiconductor wafer W1 is dipped in the treatment solution 86 in the cup 82 for a predetermined time. Consequently, the chromium film on the semiconductor wafer W1 is etched  
15 into a predetermined pattern.

After that, the relief valve 90 is opened to expose the drain path 89 and return path 91 to the atmosphere. As a consequence, the treatment solution 86 in the return path 91 is collected to the tank 85  
20 through the return path 91. Since the tank 85 is positioned below the cup 82, the treatment solution 86 in the cup 82 is also collected to the tank 85 through the supply path 88 and pump 87. After that, the support table 81 is moved down to release the  
25 semiconductor wafer W1 from fixation to the support surface by suction. In this way, the acid dip treatment by the acid dip device 72 is complete.

By the above operations, the chromium film formed on the semiconductor wafer W1 can be etched into a predetermined pattern. Also, the production of hexavalent chromium can be prevented.

5 [Application Example 6]

Application Example 6 relates to an example of a chemical treatment apparatus which uses the second chemical treatment method described previously, and by which a metal film on a semiconductor wafer is etched  
10 into a predetermined pattern as in Application Example 5. FIG. 12 is a schematic sectional view showing an example of an electrolysis device 80 of this chemical treatment apparatus. The electrolysis device 80 has substantially the same arrangement and function  
15 as the cathode electrolysis reduction device 71 shown in FIG. 10. Therefore, the same reference numerals as in the cathode electrolysis reduction device 71 shown in FIG. 10 denote the same parts in the electrolysis device 80, and an explanation thereof will be omitted.  
20 Also, the operation of the electrolysis device 80 will be described only briefly below. In the electrolysis device 80 shown in FIG. 12, a tank 13 contains a treatment solution 95 which is a halogen-ion-containing acidic treatment solution,  
25 preferably, a chloride-ion-containing treatment solution such as SAS manufactured by K.K. MURATA.

The operation of the electrolysis device 80 will

be described below.

That is, in the electrolysis device 80, similar to the cathode electrolysis reduction device 71 shown in FIG. 10, a semiconductor wafer W2 is set in  
5 a predetermined position, a support table 1 and cup 2 are integrated, and the treatment solution 95 is supplied into the cup 2. When a predetermined amount of the treatment solution 95 builds up in the cup 2, an acid electrolysis treatment is performed for the  
10 semiconductor wafer W2.

More specifically, an electric current is supplied between an anode electrode 4 and each cathode electrode 7 for a predetermined time by a power supply 19, thereby performing electrolysis reduction for  
15 a chromium film, as a cathode, of the semiconductor wafer W2 in the treatment solution 95. That is, a chromium oxide film formed on the surface of the chromium film is reduced. Then the power from the power supply 19 is stopped. The semiconductor wafer W2  
20 is kept dipped in the acidic treatment solution 95 by maintaining this state. Consequently, the chromium film on the semiconductor wafer W2 is etched into a predetermined pattern.

After that, the treatment solution 95 is collected  
25 to the tank 85, and the semiconductor wafer W2 is released from fixation to the support table 81 by suction, thereby completing the acid electrolysis

treatment by the electrolysis device 80.

By the above operation, a chromium film formed on the semiconductor wafer W2 can be etched into a predetermined pattern. Also, the production of  
5 hexavalent chromium can be prevented.

In the first and second chemical treatment methods and the apparatuses explained in [Application Example 1] to [Application Example 6] as described above, a chromium film on a carrier tape or on a  
10 semiconductor wafer can be etched into a predetermined pattern. These chemical treatment methods and chemical treatment apparatuses are similarly applicable to the formation of wiring patterns, bumps, and the like on various substrates such as a carrier tape and flexible  
15 substrate. The methods and apparatuses can also be applied to the formation of circuit patterns of, e.g., IC and LSI on a semiconductor wafer made of, e.g., silicon. The methods and apparatuses can be particularly extensively applied to technical fields in  
20 which a chromium film formed on a material is etched into a predetermined pattern.

In the apparatuses described in [Application Example 1] to [Application Example 6], a chromium film is etched. However, even when titanium, tungsten,  
25 palladium, molybdenum, and an alloy containing at least one of chromium, titanium, palladium, and molybdenum are used, these metals can be etched into

a predetermined pattern by the apparatuses of  
[Application Example 1] to [Application Example 6].  
As the alloy, nickel chrome alloy is preferably used.  
Also, the first and second chemical treatment methods  
5 are applicable not only to a metal film formed on a  
tape such as a carrier tape, but also to a metal film  
formed on a sheet. In this case, each treatment need  
only be performed in a batch manner as explained in  
[Application Example 5] and [Application Example 6].

10 Furthermore, in the apparatuses described in  
[Application Example 1] to [Application Example 6],  
a separating membrane may also be formed midway along  
the treatment solution circulating system and supply  
system. In this case, even if hexavalent chromium is  
15 produced during etching of a chromium film, the  
separating membrane prevents this hexavalent chromium  
from flowing outside as a waste solution when  
a treatment solution is collected.

20 Next, various tests conducted by the present  
inventors in relation to the above-mentioned first and  
second chemical treatment methods will be explained as  
[Experiment 1] to [Experiment 4], and the results and  
considerations of each test will be described.  
[Experiment 1]

25 In Experiment 1, the etching states of a copper  
film and chromium film were tested by making changes in  
the copper wet etching treatment, cathode electrolysis

reduction treatment, and acid dip treatment according to the chemical treatment methods described above, and by changing various conditions of these treatments. FIG. 13 shows the results of Experiment 1.

5           Referring to FIG. 13, as a material to be treated in Experiment Nos. 1 and 2, a material obtained by forming a chromium film and copper film in this order on a piece of a polyimide tape was used. Also, as a material (sample) to be treated in Experiment Nos. 3  
10 to 8, a material obtained by forming a chromium film on a piece of a polyimide tape and forming a copper film etched into a predetermined pattern on this chromium film was used. In FIG. 13, "Simultaneous (A)" indicates that the copper wet etching treatment and  
15 acid dip treatment were performed by using the same treatment solution without performing any cathode electrolysis reduction treatment. "Individual (B)" indicates that the copper wet etching treatment and the cathode electrolysis reduction treatment and/or the  
20 acid dip treatment were individually performed, i.e., indicates that the cathode electrolysis reduction treatment and/or the acid dip treatment was performed after the copper wet etching treatment. "Anode electrolysis oxidation (C)" indicates that instead of  
25 the cathode electrolysis reduction treatment, electrolysis oxidation was performed in a predetermined treatment solution by using a material to be treated as



an anode, thereby oxidizing a chromium film. In the columns of "Cu peeling" and "Cr peeling" in the upper right corner of FIG. 13, the etching states of the copper film and chromium film are indicated by "○" or "×". "○" or "×" was determined on the basis of whether the piece of the polyimide tape was visually confirmed after each treatment.

In Experiment Nos. 1 and 2, the copper film was etched into a predetermined pattern, but the chromium film was not. This means that even when the copper wet etching treatment and acid dip treatment are simultaneously performed by using the same treatment solution, a chromium film cannot be etched into a predetermined pattern simultaneously with a copper film.

In Experiment Nos. 3 to 6, the chromium film was not etched when the dip, anode electrolysis oxidation, and cathode electrolysis reduction treatments were independently performed.

In Experiment No. 7, the chromium film was etched when the cathode electrolysis reduction treatment and acid dip treatment were performed for a material to be treated. More specifically, the chromium film was etched into a predetermined pattern when a material to be treated was used as a cathode to perform electrolysis reduction in SAS manufactured by K.K. MURATA as a treatment solution containing chloride ion,

and the material was dipped in the same treatment solution. Note that as the conditions of Experiment No. 7, "treatment solution concentration (vol%) 50/50", "current density ( $A/dm^2$ ) 5/", "temperature ( $^{\circ}C$ ) 30/30",  
5 and "time (sec) 2/8 and 5/8" indicate that the treatment solution concentration was 50 vol%, the current density was 5  $A/dm^2$ , the treatment solution temperature was  $30^{\circ}C$ , and the treatment time was 2 and 5 sec in the cathode electrolysis reduction process,  
10 and that the treatment solution concentration was 50 vol%, the treatment solution temperature was  $30^{\circ}C$ , and the treatment time was 8 sec in the acid dip process.

In Experiment No. 8, the chromium film was not  
15 etched when sodium bisulfite was added as a reducing agent to the treatment solution. That is, a chromium film cannot be etched even when dip is simply performed by adding a reducing agent in order to reduce a chromium oxide film formed on the surface of  
20 the chromium film, without performing any cathode electrolysis reduction process for reducing the oxide film.

#### [Experiment 2]

In Experiment 2, to more specifically verify the  
25 results of Experiment No. 7 of Experiment 1, the etching state of a chromium film was tested by changing the various conditions of Experiment No. 7 of

Experiment 1. FIG. 14 shows the results of

Experiment 2. As a material to be treated, a material  
obtained by forming a chromium film on a piece of  
a polyimide tape and forming a copper film etched into  
a predetermined pattern on this chromium film was used.

In the column of "Cr peeling" in the upper right  
corner of FIG. 14, "○" means that a chromium film was  
etched. This was determined if the piece of the  
polyimide tape was visually confirmed after each  
treatment.

In Experiment No. 1, the chromium film was etched  
into a predetermined pattern even when the cathode  
electrolysis reduction treatment was performed at  
a relatively low current density of  $1 \text{ A/dm}^2$ .

In Experiment No. 2, the treatment time shortened when  
the current density was increased to  $5 \text{ A/dm}^2$ , i.e.,  
when the current density was made higher than that in  
Experiment No. 1.

In Experiment Nos. 3 to 6, the chromium film was  
etched into a predetermined pattern even when the acid  
dip treatment and cathode electrolysis reduction  
treatment were performed at a relatively low treatment  
solution concentration of 5 vol%.

In Experiment Nos. 3 to 8, the treatment time  
shortened when the treatment solution concentration was  
increased in the acid dip treatment and cathode  
electrolysis reduction treatment. This means that

the treatment solution concentration is related to the treatment speed.

[Experiment 3]

5 In Experiment 3, on the basis of Experiment No. 7 of Experiment 1 and Experiment 2, whether reduction of chromium on the surface of a chromium film occurs under the influence of an acidic treatment solution containing chloride ion in the cathode electrolysis reduction process was verified. More specifically, in 10 the cathode electrolysis reduction process, the cathode electrolysis reduction treatment was performed by using a NaCl solution as a neutral treatment solution containing chloride ion, instead of an acidic treatment solution containing chloride ion. After that, the 15 etching state of the chromium film was tested by omitting the acid dip process or by performing the acid dip process. FIG. 15 shows the results of Experiment 3. As a material to be treated, a material obtained by forming a chromium film on a piece of 20 a polyimide tape and forming a copper film etched into a predetermined on this chromium film was used.

In the column of "Cr peeling" in the upper right corner of FIG. 15, the etching state of the chromium film is indicated by "O" or "X". "O" or "X" was 25 determined on the basis of whether the piece of the polyimide tape was visually confirmed after each treatment.

In Experiment No. 1, the chromium film was not etched when only the cathode electrolysis reduction treatment using the NaCl solution as a neutral treatment solution containing chloride ion was performed. Compared to Experiment No. 1 as a control experiment, in Experiment No. 2, the chromium film was etched into a predetermined pattern when the cathode electrolysis reduction treatment using the NaCl solution as a neutral treatment solution containing chloride ion and the dip treatment using SAS manufactured by K.K. MURATA were performed in this order.

Experiment No. 2 reveals that a chromium film can be etched into a predetermined pattern even when a cathode electrolysis reduction treatment using a neutral treatment solution containing chloride ion, instead of an acidic treatment solution containing chloride ion, is performed. That is, not only an acidic treatment solution containing chloride ion but also a neutral treatment solution containing chloride ion can be applied to the cathode electrolysis reduction process. This probably indicates that chromium oxide on the surface of a chromium film in the treatment solution is reduced not under the influence of the acidic treatment solution containing chloride ion but under the influence of hydrogen in the treatment solution.

[Experiment 4]

In Experiment 4, the pH dependence of a treatment solution in the cathode electrolysis reduction process was verified. More specifically, in the cathode electrolysis reduction process, the cathode electrolysis reduction treatment was performed by using a treatment solution obtained by adding NaOH to an NaCl solution as a neutral treatment solution containing chloride ion, instead of an acidic treatment solution, thereby changing the pH of this NaCl solution to 5, 7, 9, and 10. After that, the etching state of a chromium film was tested by performing the acid dip process. FIG. 16 shows the results of the experiments.

As a material to be treated, a material obtained by forming a chromium film on a piece of a polyimide tape was used. In the column of "Cr peeling" in the upper right corner of FIG. 16, the etching state of the chromium film is indicated by "O" or "X". "O" or "X" was determined on the basis of whether the piece of the polyimide tape was visually confirmed after each treatment. The results of Experiment Nos. 1 to 4 reveal that a chromium film can be reliably etched regardless of whether the pH is neutral or alkaline.

[Experiment 5]

In Experiment 5, whether hexavalent chromium was present in treatment solutions of the chemical treatment methods of the present invention was detected

by using hydrochloric acid, sulfuric acid, and  
a neutral NaCl solution as the treatment solutions.  
Note that chromium including trivalent chromium and  
hexavalent chromium was detected by general flame  
5 atomic absorption spectrometry, and hexavalent chromium  
was detected by using general diphenylcarbazide  
absorption spectrophotometry. As a material to be  
treated, a material obtained by forming a chromium film  
on a piece of a polyimide film and forming a copper  
10 film etched into a predetermined pattern on this  
chromium film was used. FIG. 17 shows the results of  
Experiment 5.

Referring to FIG. 17, "Chromium (D)" indicates  
trivalent chromium and hexavalent chromium in each  
15 treatment solution.

FIG. 17 shows that chromium was detected in all of  
the hydrochloric acid, sulfuric acid, and neutral NaCl  
solution. However, although hexavalent chromium was  
detected in the sulfuric acid, almost no or entirely no  
20 hexavalent chromium was detected in the hydrochloric  
acid and NaCl solution. When the neutral NaCl solution  
was used as a treatment solution in the acid dip  
process, the chromium film was not etched into  
a predetermined pattern. On the basis of these  
25 results, Experiment 5 reveals that almost no or  
entirely no hexavalent chromium is produced when  
an acidic treatment solution containing chloride ion is

used as a treatment solution in the acid dip process.

Examples 1 and 2 will now be explained below as practical examples of the chemical treatment methods described above.

5 (Example 1)

One surface of a 25- $\mu$ m thick polyimide film was coated with a 500-Å thick metal chromium film by sputtering and then coated with a 1- $\mu$ m thick copper film by the same method. After that, the polyimide film surface coated with these chromium film and copper film was further coated with a 7- $\mu$ m thick copper film, thereby preparing a film carrier tape having a copper film thickness of 8- $\mu$ m. On this film carrier tape, a predetermined circuit pattern was formed by a predetermined method by using a photoresist dry film, thereby forming an etching resist film.

Subsequently, the copper film was etched by dip under conditions (1) presented below, thereby obtaining a film carrier tape having the predetermined circuit pattern. The chromium of the chromium film was not etched away but remained as a residue on the polyimide film surface.

(1) Etching conditions

Etching solution	...A-process (manufactured by Meltex K.K.)
Bath temperature	...50 $\pm$ 1°C
pH	...8.1 to 8.5



Copper concentration ... $140 \pm 5$  g/L

Treatment time ...30 sec

During the etching treatment, the etching solution was agitated while the material to be treated was shaken.

The surface of the chromium film was then reduced by performing a cathode electrolysis reduction treatment for the chromium film under conditions (2) presented below.

(2) Cathode electrolysis reduction treatment conditions

Treatment solution ...SAS (manufactured by K.K. MURATA)

Treatment solution concentration...50 mL/L

Bath temperature ... $30 \pm 1^\circ\text{C}$

Polarity ...material to be treated was cathode

Current density ... $2 \text{ A/dm}^2$

Electrolysis time ...3 sec

Subsequently, the chromium of the chromium film was etched away by performing an acid dip treatment under conditions (3) presented below.

(3) Acid dip treatment conditions

Treatment solution ...SAS (manufactured by K.K. MURATA)

Treatment solution concentration...500 mL/L

Bath temperature ... $30 \pm 1^\circ\text{C}$

Treatment time ...15 sec

(Example 2)

Treatments were performed following the same procedures as in Example 1 until a copper film on one surface of a polyimide film similar to that of Example 1 was etched. As in Example 1, after the copper film was etched, the chromium of a chromium film was not etched but remained as a residue on the polyimide film surface.

Next, a cathode electrolysis reduction treatment and acid dip treatment were simultaneously performed for the chromium film under conditions (4) presented below. That is, the cathode electrolysis reduction treatment was performed for a predetermined time while the material to be treated was dipped in the treatment solution. Consequently, the surface of the chromium film was reduced, and chromium was immediately dissolved in the treatment solution and removed from the polyimide film. That is, the surface of the chromium film was reduced and the chromium film was etched in the treatment solution in the same process.

(4) Conditions of cathode electrolysis reduction treatment and acid dip treatment

Treatment solution ...SAS (manufactured by

K.K. MURATA)

Treatment solution concentration...500 mL/L

Bath temperature ...30  $\pm$  1°C

Treatment time           ...15 sec  
Polarity                   ...material to be treated was  
                                  cathode  
Current density           ...2 A/dm<sup>2</sup>

5           Additional advantages and modifications will  
readily occur to those skilled in the art. Therefore,  
the invention in its broader aspects is not limited to  
the specific details and representative embodiments  
shown and described herein. Accordingly, various  
10           modifications may be made without departing from the  
spirit and scope of the general inventive concept as  
defined by the appended claims and their equivalents.